

# How Does Streamflow Affect Metals in the Upper Arkansas River?



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## INTRODUCTION

Large quantities of metallic minerals in several Western States, including Colorado, were deposited during the formation of the Rocky Mountains. As a result of these natural deposits, mining districts in the upper Arkansas River Basin have been active in Colorado for more than 100 years, producing large quantities of copper, gold, lead, silver, and zinc.

Metal deposits generally contain large amounts of sulfur, which are closely tied to the chemical formation of metal-sulfide minerals. Mining increases the exposure of metal sulfides to water and oxygen and accelerates the natural acid-producing weathering process. In this process, the iron and sulfur components in pyrite are oxidized and produce acidity ( $H^+$ ). The release of acidity lowers the pH of the drainage water. Metals are more mobile under acidic conditions and can be released from the drainage water to the receiving stream in high concentrations, producing a condition known as acid mine drainage.

Water quality in the upper Arkansas River, between Leadville and Pueblo Reservoir (fig. 1), has been substantially degraded by historic mining activity (Moran and Wentz, 1974; Wentz, 1974). Water flowing through abandoned mines and tailings piles, primarily in the Leadville area, has contributed high concentrations of cadmium, copper, lead, zinc, and other metals to the upper Arkansas River.

Beginning in 1990, a study was done by the U.S. Geological Survey, in cooperation with several local agencies, to evaluate the effects of streamflow regime on dissolved-metal speciation in the upper Arkansas River. This evaluation is needed for water managers to more accurately assess the relative bioavailability and potential toxicity of these metals to aquatic organisms in the upper Arkansas River. This fact sheet describes how streamflow affects selected metal concen-



Figure 1. Location of study area and sampling sites.

trations and speciation of these metals in the upper Arkansas River between Leadville and Portland, Colorado. A more thorough discussion of the results of this study is presented in Clark and Lewis (in press).

## Do Metals Pose a Toxicological Risk to Aquatic Life?

In trace amounts, some metals are essential to life. Some common examples include copper, iron, and zinc. Other

metals, including cadmium, have no known biological function. However, most metals become toxic in high concentrations. Acid mine drainage can produce metal concentrations and acidity that are high enough to be toxic to aquatic life. Cadmium, copper, lead, and zinc are metals of particular concern because of their toxicity to aquatic life. Acute exposure (short-term, high concentration) of these metals can kill organisms directly, whereas chronic exposure (long-term, low concentration) can result in either mortality or nonlethal effects such as stunted growth, reduced reproduction,



deformities, or lesions (U.S. Fish and Wildlife Service, 1993).

Historically, metal concentrations in the upper Arkansas River have exceeded water-quality standards (Colorado Department of Health, 1994). High concentrations of cadmium, copper, and zinc in the upper Arkansas River might be one cause for an increase in the mortality rate of brown trout (U.S. Fish and Wildlife Service, 1993). In the spring of 1992, water-treatment plants were constructed at two mine-drainage tunnels to help mitigate the elevated metal concentrations. The frequency of exceedance of water-quality standards for all metals has decreased since their operations began (Clark, 1996).

## ***Metals in the Hydrologic System***

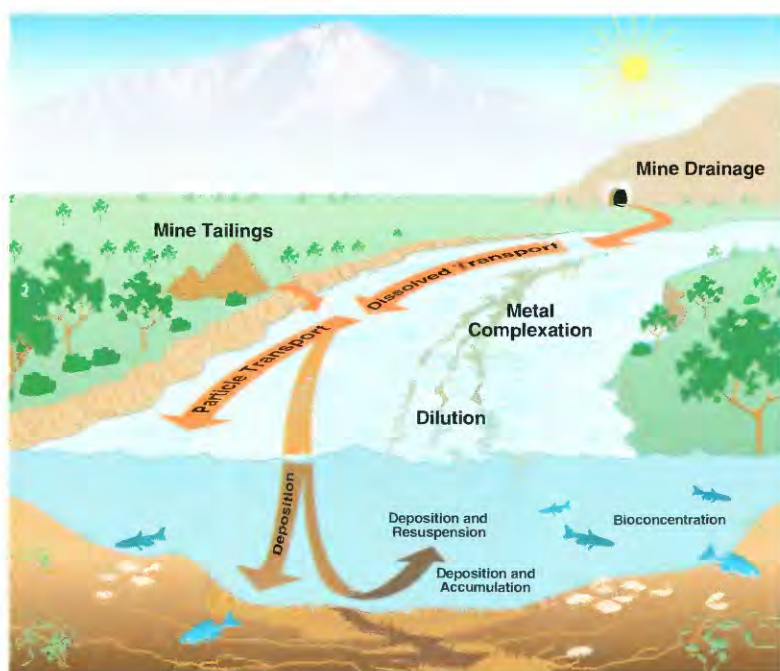
Metals can take many pathways through the environment (fig. 2). Metal sources can include point sources, such as mine-drainage tunnels, or nonpoint sources, such as widely dispersed mine tailings or waste piles. Once in the water, metals can be in dissolved or particulate forms. The metals can become sorbed to sediments and can settle under gravity close to the metal sources. During high

flows, like snowmelt runoff, the metal-laden sediments can be resuspended and transported farther downstream. Dissolved metals remain in the water column and can be transported over long distances, potentially affecting water quality many miles downstream from the metal sources. The toxicity of metals is related not only to their concentration, but also to their form. The uptake of metals from the dissolved phase of the water column generally is the pathway that is most toxic to aquatic life (Gerhardt, 1993).

Within the dissolved phase, metals can exist as different forms or "species." Dissolved metals can exist by themselves as free-metal ions or they can form complexes with other constituents in the water (such as carbonates, chlorides, and sulfates). For example, dissolved cadmium can exist as the free-metal ion  $\text{Cd}^{+2}$  or it can combine with carbonate ( $\text{CO}_3^{-2}$ ) to form dissolved cadmium carbonate ( $\text{CdCO}_3$ ). There is an increased potential that the dissolved-metal ion will become bound by a complexing agent rather than exist in the free-metal ion form when there are more complexing agents in the water. Most studies of metal toxicity have indicated that the free-metal ion is the more toxic dissolved-metal species (Florence, 1982).

Alkalinity and pH affect the speciation of dissolved metals in natural water. Alkalinity is a measure of the water's ability to neutralize acid. The principal complexing agents that constitute alkalinity are the dissolved carbon dioxide species. The carbon dioxide species are available to form complexes with dissolved metals. The pH of a solution is the hydrogen-ion activity. An acidic solution has a pH less than 7, a neutral solution has a pH of 7, and a basic solution has a pH greater than 7. Low alkalinity and pH are more conducive to the existence of free-metal ions in solution.

In the upper Arkansas River, alkalinity and pH vary with streamflow. The high streamflow during snowmelt runoff typically has lower alkalinity and pH than low streamflow. Another factor affecting alkalinity and pH in the Arkansas River is that water imported into the river from the Colorado River Basin (transmountain water) generally has lower alkalinity and pH than native water. Since most of the transmountain water is routed through Twin Lakes Reservoir and Lake Creek to the Arkansas River, the main-stem reach immediately downstream from the confluence of Lake Creek and the Arkansas River is most susceptible to being affected by the chemistry of the transmountain water.



**Figure 2.** Metal cycling and transport in an aquatic environment.

## **METAL SPECIATION IN THE ARKANSAS RIVER**

From April 1990 through March 1993, 207 water samples were collected from eight sites on the Arkansas River between Leadville and Portland, Colorado (fig. 1), for analysis of concentrations of dissolved metals. The water samples were collected during different streamflow regimes: (1) early-snowmelt runoff (April), (2) peak-snowmelt runoff (May-June), (3) post-snowmelt runoff (July-September), and (4) low flow (October-March). The water samples were analyzed for concentrations of dissolved cadmium, copper, lead, and zinc (Dash and Ortiz, 1996). Unfortunately, an analysis of free-metal ion concentrations is not routinely possible in most water-quality sampling programs, and metal concentrations typically are



reported as dissolved (filtered) or total (unfiltered). However, computer models exist that can calculate the speciation of these dissolved-metal concentrations and provide more insight into the relative bioavailability and potential toxicity of dissolved metals in the water column. The computer model MINTEQA2 (Allison and others, 1991) was used for metal-speciation analysis in this study.

## Cadmium and Zinc

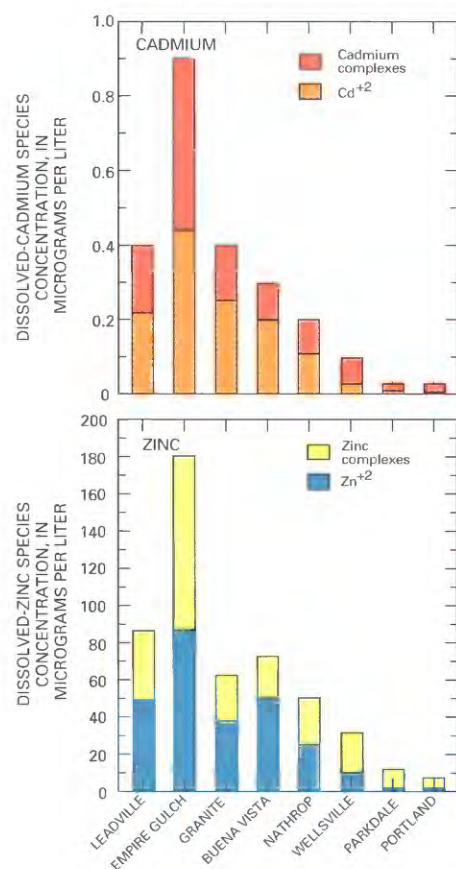
Although the magnitude of the concentrations of dissolved cadmium and zinc are different (less than a few micrograms per liter compared to hundreds of micrograms per liter, respectively), their concentrations had similar spatial patterns (fig. 3). The highest concentrations of dissolved cadmium and zinc were at Empire Gulch, which is immediately downstream from the primary mine-drainage sources. Concentrations decreased more than 50 percent between

Empire Gulch and Granite, largely because of dilution by Lake Creek (fig. 1), which has relatively low metal concentrations.

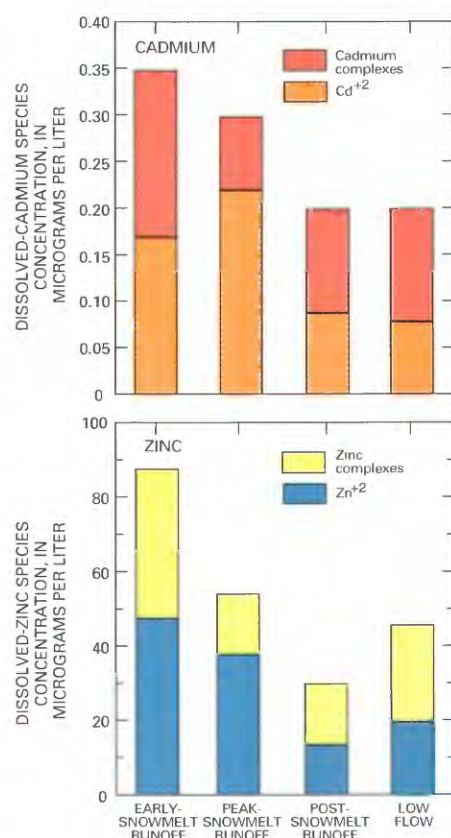
The free-metal ions ( $\text{Cd}^{+2}$  and  $\text{Zn}^{+2}$ ) dominated the speciation from Leadville to Nathrop, whereas the cadmium and zinc complexes dominated the speciation from Wellsville to Portland. More than 60 percent of the dissolved species occurred as free-metal ions at Granite and Buena Vista. The low alkalinity and dissolved-solids concentration of the inflow from Lake Creek resulted in low metal-complexing potential of the river and a high percentage of free-metal ions at Granite and Buena Vista, compared to upstream sites.

Dissolved cadmium and zinc concentrations also were similar in relation to streamflow regime in the Arkansas River (fig. 4). The highest concentrations of dissolved cadmium and zinc were during early-snowmelt runoff. During early-snowmelt runoff, streamflow begins to

increase as lower elevation snow melts and flushes the abandoned mines, mine dumps, and tailings piles of metal-enriched water. The volume of water that actually flows into the river during early snowmelt is relatively small, but because the flow of the river is low, the effect on metal concentrations can be substantial. Dissolved-metal concentrations become diluted by large volumes of snowmelt during peak-snowmelt runoff in May and June. Although metal concentrations decreased during peak-snowmelt runoff, the percentage of dissolved cadmium and zinc represented by their free-metal ions increased. The lower alkalinity and lower pH of snowmelt water tends to favor the speciation of the free-metal ions compared to the metal complexes; about 70 percent of the dissolved cadmium and zinc existed as free-metal ions during snowmelt runoff. In contrast, less than 50 percent of the dissolved cadmium and zinc existed as free-metal ions during the post-snowmelt and low-flow periods, when alkalinity and pH generally were higher.



**Figure 3.** Median concentrations of dissolved cadmium and zinc species by sampling site, April 1990–March 1993.

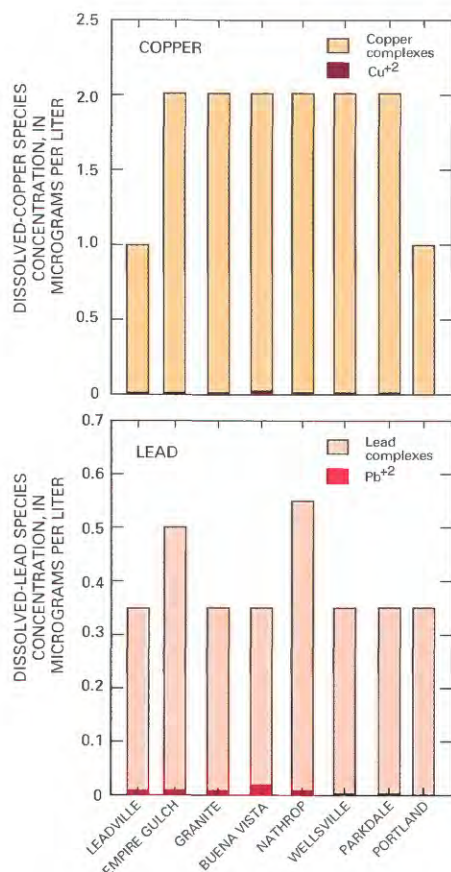


**Figure 4.** Median concentrations of dissolved cadmium and zinc species by streamflow regime, April 1990–March 1993.

## Copper and Lead

Dissolved-copper and lead concentrations exhibited less spatial variability than cadmium and zinc. Concentrations varied little between Leadville and Portland (fig. 5) because a large percentage of the samples contained low concentrations, which were about equal to or less than the minimum laboratory reporting levels of 1 microgram per liter for copper and 0.5 microgram per liter for lead. At all sites, the speciation of dissolved copper and lead was dominated by complexed species. The water-quality conditions in the Arkansas River favor the complexation of dissolved copper and lead over the existence of their free-metal ions ( $\text{Cu}^{+2}$  and  $\text{Pb}^{+2}$ ); less than 5 percent of the dissolved-copper and lead concentrations occurred as free-metal ions. Dissolved-copper and lead concentrations tended to be highest during peak-snowmelt runoff. However, because of the high-complexing nature of copper and lead, the lower pH and lower alkalinity of snowmelt had less effect on copper and lead speciation than it had on cadmium and zinc. Similarly, inflow from Lake Creek had less effect on copper and lead speciation.



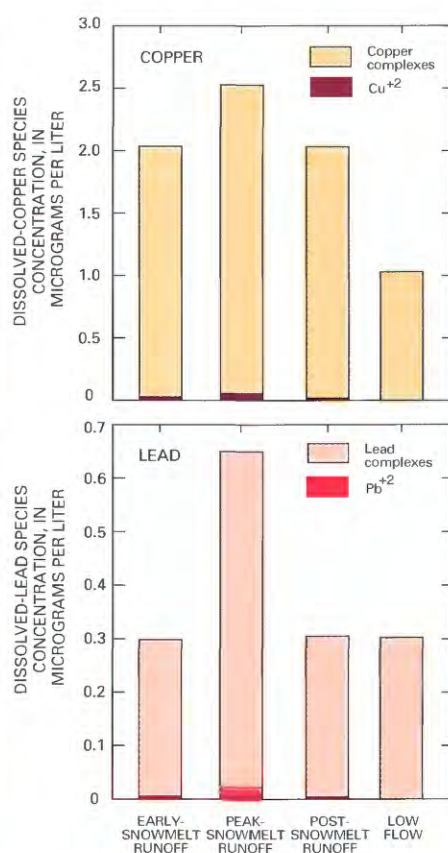


**Figure 5.** Median concentrations of dissolved copper and lead species by sampling site, April 1990–March 1993.

## SIGNIFICANCE OF METAL SPECIATION TO WATER QUALITY

Model calculations with MINTEQA2 indicated the most dominant species of dissolved cadmium and zinc were their free-metal ions, whereas dissolved copper and lead were almost completely complexed. From an aquatic-life perspective, this indicates that dissolved-cadmium and zinc concentrations might be more available to aquatic life in the upper Arkansas River Basin than dissolved-copper and lead concentrations.

The U.S. Fish and Wildlife Service (1993) expressed concerns that metal toxicity to aquatic life might be increased by the importation of transmountain water with low metal-complexing potential. The model results indicate that a high percentage of dissolved metals, particularly cadmium and zinc, existed as free-metal ions in the reach immediately down-



**Figure 6.** Median concentrations of dissolved copper and lead species by streamflow regime, April 1990–March 1993.

stream from the confluence of Lake Creek and the Arkansas River, where most transmountain water enters the Arkansas River. However, the inflow from Lake Creek also dilutes metal concentrations, effectively decreasing their potential toxic effects.

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Information on technical reports and hydrologic data related to this study can be obtained from:

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